ORIGIN OF MACRO-GROWTH FEATURES ON THE BASAL SURFACES OF SYNTHETIC QUARTZ MONOCRYSTALS*

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(*Received May 2, 1968*)

(Plate 15)

ABSTRACT. Growth spires, both right-handed and left-handed, and growth terraces, were observed on the basal surfaces of quartz seed plates grown hydrothermally for short periods of time. Step heights of individual turns of three spires and ledges of one terrace were measured carefully by the depth of focus method, and were found to be in the range 0.01—0.001 mm. The origin of these macro-growth features has been discussed.

INTRODUCTION

Some quartz monocrystals grown in this laboratory during routine investigations revealed very well-defined surface growth features comprising of steep spires and terraces on some large hillocks visible even at low magnification. A careful appraisal of the characteristics of these features made it clear that they formed under rather unusual circumstances. An attempt has been made in this paper to explain some of these features on the basis of data available on deformation characteristics of quartz.

EXPERIMENTAL METHODS

Experimental techniques of growing quartz monocrystals are quite well known. Full details of the method used, description of the growth morphological features, and effects of constraints on growth, of some of the crystals synthesized were presented in a series of papers from this laboratory (Bandyopadhyay and Saha, 1966a; 1966b; 1967). Growth conditions of the crystals selected for this study were :

(i) Growth temperature $= 323^\circ \pm 3^\circ$C; Pressure $= 5{,}500 \pm 500$ psi; Duration $\simeq 1$ day; Basal growth rate $= 7$ mils/day.

(ii) Growth temperature $= 300^\circ \pm 5^\circ$C; Pressure $= 5{,}500 \pm 500$ psi; Duration $\simeq 4$ days; Basal growth rate $= 12$ mils/day.

*Paper presented at the "International Conference on Characterization of Materials" held at the Pennsylvania State University, University Park, Pa., USA, in November 1966. Reproduced here in slightly modified form.

Both experiments were carried out with processed flawless basal seed plates cut from natural quartz, kindly provided by M/s Bharat Electronics Ltd. The growth rates were very low compared to what were obtained normally (Bandyopadhyay and Saha, 1966a), and the runs were switched off after relatively short periods of time. Consequently faces other than basal, (0001), had little chance to develop (Bandyopadhyay and Saha, 1966b), and the basal hillock densities were also considerably higher (Bandyopadhyay and Saha, 1965).

The grown crystals were first dipped in conc. hydrofluoric acid for a few seconds and then thoroughly rinsed in distilled water and dried. The basal surfaces were observed under the microscope and interesting growth features were photographed.

Surface contourings of some of the large basal hillocks were carried out by the depth of focus method using a Leitz Ortholux-Pol Microscope with a very accurately graduated vertical movement. This instrument has very negligible backlash, so that any error in measurement would mainly be due to (*i*) rather rough nature of the surfaces of the growth features, sometimes making it difficult to obtain proper focussing, (ii) rather poor visibility, in portions, of the boundaries demarcating the turns of the spires and ledges of the terraces, (iii) observers' personal error. Four readings, two by each of the authors, were taken of each point, and the average computed. The limits of error stated in table 1 were estimated from the maximum range of variation obtained for the four readings.

The data obtained were utilized in preparing enlarged topographical maps of the hillocks and drawing appropriate sections. Approximate step heights of spires and terraces were found by dividing the overall height of the hillocks from central apex to base of lowermost discernible turn of spire or terrace, by the total number of turns.

RESULTS

Figures 1(a) and 1(b) (plate 15A) and figure 2 (plate 15B) are photographs of opposite basal surfaces of the same crystal. Two left-handed spires (L_1, L_2), one right-handed spire (R_1) and one terraced hillock (T_1) in figure 1(a), and one left-handed spire (L_3) and two right-handed spires (R_2, R_3) in figure 2 are very prominent**. All these hillocks belong to the type II category (Bandyopadhyay and Saha, 1966b).

Most of the other hillocks do not exhibit such prominent growth features, but faint traces can be discerned in some other hillocks.

Measurements of step heights of a few of those spires and terraces by the depth of focus method (described in the preceding section) are given in table 1.

**Biot's convention has been followed here.

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PLATE 15 A

igure a. Basal surface of a grown quartz crystal (No. 48) showing two left-handed spires, one right-handed spire and one terraced hillock

Figure 1. (b) Oppositely oriented spires on coalescing growth hillocks; enlarged view of R_1 of figure 1 (a).

Indian Journal of Physics
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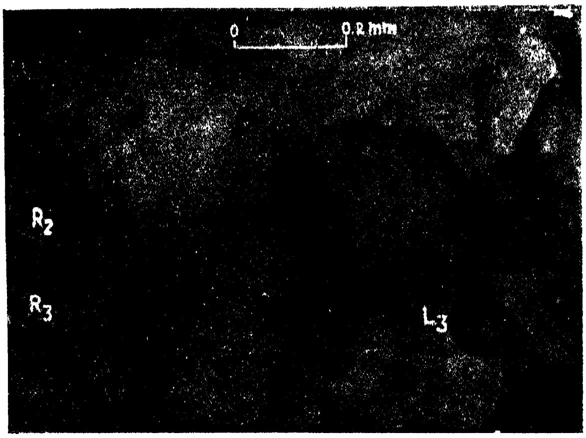

Figure 2. The opposite basal surface of the same quartz crystal (No. 48) showing one left-handed spire and two right handed spires.

Figure 3. Basal surface of a grown quartz crystal (No. 49) showing the reversed orientation of triangular hillock in optically twinned patch.

Table 1

Hillock designation	Nature of hillock	No. of growth units per hillock	Total height of hillock (mm)	Step height (mm)
T_1	Terrace	Two ledges	0.01503 $\pm$0.00200	0.00751
L_1	Left-handed spire	Five turns	0.01368 $\pm$0.00200	0.00233
L_3	Left-handed spire	Four turns	0.01929 $\pm$0.00200	0.00482
R_2	Right-handed spire	Four turns	0.01008 $\pm$0.00200	0.00252

In most cases thicknesses of individual turns of spires or terraces of each hillock contoured were found to be more or less uniform within the estimated limits of error. Only spire L_3 (figure 2, plate 15B) showed marked variation in thickness at the two opposite ends of the same turn.

OBSERVATIONS

The features which emerge as very significant from examination of the surface features of grown basal seed plates of quartz and measurements of step heights of spires and terraces on them are :

(A) Presence of both right-handed and left-handed spires on hillocks (type II) of the same basal surface (figures 1 and 2, plate 15).

(B) Enormous step heights of individual turns of spires and ledges of terraces (table 1).

(C) Variable step heights of different spires on the same basal surface (L_3 and R_2, table 1).

(D) Curved edges of individual turns of spires and ledges of terraces (figures 1 and 2, plate 15).

(E) Occurrence of a terrace with a single central point (T_1, figure 1, plate 15A).

(F) An approximate multiplicity of the step heights of 0.0025 mm. or 2.5μ

Those features should be taken into consideration in discussing the probable mode of origin of large type II growth hillocks on the basal surfaces of quartz monocrystals.

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DISCUSSIONS

Failure of the theory of two-dimensional nucleation and growth to explain growth of iodine crystals from the vapour phase at low supersaturations (Frank, 1949; Van Hook, 1961) provided the incentive for looking for an alternative mode of crystal growth. This was first proposed by Frank (1949), who showed that (i) growth spires of unit step height are generated at screw dislocations, the hand of the spire depending upon the sign of the screw dislocation, and that (ii) isolated pairs of screw dislocations of opposite signs can give rise to closed loop terraced structures, as long as the distance between the two spires of a pair exceeds the diameter of the critical two-dimensional nucleus required for that supersaturation. Numerous evidences were obtained in its favour (Griffin, 1950; 1951; Verma, 1951; Amelinckx, 1952a; 1952b).

The first reported instance of growth influenced by dislocation was proved by multiple-beam interferometric method to be composed of monomolecular steps (Griffin, 1950; 1951). In organic crystals, where the lattice constants of the unit cell itself are usually quite large, growth by the spiral mechanism was clearly demonstrated (Dawson and Vand, 1951). Striking evidences of growth spires, mostly in silicon carbide, were later discovered, which were found to be composed not of monomolecular layers, but multiples of it (Krishna and Verma, 1962; Singh and Verma, 1964; Forty, 1951). This was explained by polytypism (Frank, 1951), and Verma and Krishna (1966) were able to synthesize a polytype of silicon carbide whose unit cell was made up of 594 basic units (thickness of monomolecular layer $\simeq$ 1500Å). Growth spire of such a polytype would therefore be easily observable under the microscope.

Polytypism is favoured by certain layered structures which usually possess a very prominent slip plane on which translation and/or rotation can occur, such as SiC, ZnS, CdI_2, graphite, micas, clays, and a host of other minerals and compounds. But if we consider the crystal structure of α-quartz, it immediately becomes obvious that the situation is entirely different here. It is a tectosilicate structure where each SiO_4 tetrahedron is linked to its neighbouring SiO_4 tetrahedra at each of its four corners, and all Si-O bonds are of equal strength though the different Si-O-Si bond angles can vary to some extent. Thus it is difficult to conceive of a set of weak planes in this structure that can give rise to polytypism, and thereby explain the enormous step heights of the spires and terraces on the basal surfaces of synthetic quartz monocrystals.

Evidences of another mechanism of formation of thick growth layers were obtained by Sunagawa (1962). Thin growth layers originate from groups of dislocations arranged along a line and then coalesce during propagation to form thick layers which may even be a few hundred Å thick. But every basal hillock of quartz showing spiral or terraced structure possesses a single central apex (figures 1 and 2, plate 15), and it is difficult to conceive of a row of dislocations in such cases. Neither does the mechanism of bunching of growth layers (Cabrera and Vermilyea, 1958; Frank, 1958) appear to be very plausible, at least for the basal surfaces of the grown seed plates illustrated in figures 1 and 2, plate 15, since then all the hillocks should normally exhibit spires or terraces. The growth environment of the synthetic quartz crystals inside the autoclaves was so uniform that any kind of shock (i.e. a thermal shock) should affect the whole of the surface of the crystal being grown. Recently, formation of screw dislocations by the capture of foreign particles has been reported by Kozlovskii (1962), and growth layers of thicknesses 1000-2000Å have been detected. But from data on precipitation of impurities on grown quartz crystals that have been obtained, it can be inferred that macro-growth features of the types which are under discussion are not generated at those impurity centres (Bandyopadhyay and Saha, 1967, figures 16-18).

There cannot be any doubt that some crystallographic control is always maintained on growth. Its manifestation can be seen in the pronounced trigonal symmetry of many of the growth hillocks. The orientation of the triangular hillocks becomes reversed in the optically twinned patches (figure 3, plate 15B). But the existence of both right-handed and left-handed spires on the same basal surface clearly establishes the dominating influence of dislocations in controlling and promoting growth. However, none of the above suggested mechanisms helps us to find a suitable explanation for the origin of macro-growth layers on basal surfaces of synthetic quartz monocrystals. Attention was therefore directed to a critical examination of the deformation characteristics of quartz single crystals.

DEFORMATION CHARACTERISTICS OF QUARTZ

Brace (1963) carried out some experiments on deformation of natural and synthetic quartz at room temperature. Using a pyramidal indenter and light load, he was able to produce non-recoverable deformation characterized by :(i) permanent depression at the centre of the indented region, (ii) open non-crystallographically oriented cracks rimming the indent and extending locally into surrounding material, and (iii) sets of parallel markings within the indents (depressed regions) having small shear offsets, nearly parallel to the three faces $\{1\bar{1}01\}$, whose extent at depth could not be determined. At heavy loads, or when the lengths of the indents exceeded 100μ, spalling and wholesale fracturing around the indents took place. Brace concluded that within the deformed region quartz apparently behaved in a 'ductile' fashion when indented lightly, but from various considerations argued that the parallel markings in the depressed regions should rather be regarded as sets of systematic microfractures, and that a fracture mechanism rather than a slip mechanism was responsible for the apparent ductility.

Christie *et al.* (1964) studied experimental deformation of single crystals of quartz at high confining pressure of 27-30 Kb., and at 24°C. They observed that the samples failed by rupture along some crystallographically controlled 'faults' parallel to the basal, rhombohedron and prism surfaces of quartz. After a careful consideration of the nature of these 'faults' and the associated deformation features they concluded that the faults were apparently a fracture phenomenon. But the most satisfactory explanation of the crystallographic nature of the 'faults' was found by assuming that the cracks were initiated by yielding and slight plastic flow on certain planes and then propagated rapidly by brittle fracture mechanism. Thus this idea agrees fully well with the conclusion suggested by Brace (1963), that the parallel lines in the deformed regions of quartz are sets of systematic microfractures rather than any slip planes.

Recently McLaren and Phakey (1965a, 1965b) examined quartz single crystals of different degrees of perfection and purity by transmission electron microscopy and selected area diffraction. Fracture marks, accompanied by some misorientation, were observed in citrine quartz, and it was concluded that quartz remains perfectly elastic under stress until fracture occurs. In another instance, positive evidences of arrays and networks of dislocations on both basal and $(10\bar{1}1)$ planes were obtained only in natural milky quartz. It was concluded that the dislocation substructures were produced by creep over very long periods of time. Imperfect nature of the specimen used suggests that the quartz might possibly have undergone the reversible $\alpha \rightleftharpoons \beta$ phase transformation at some stage of its history, and this might be another factor contributing towards the formation of the dislocation substructures.

CONCLUSION

Experimental data available on deformation of quartz monocrystal at room temperature suggest that (i) this mineral on the whole remains elastic under stress until fracture occurs, (ii) evidences gained in favour of plastic deformation were rather inconclusive, and even if plastic deformation did occur, its range of operation was very narrow and restricted, (iii) sets of parallel markings that developed should be regarded as systematic microfractures rather than sets of slip planes. A possible mechanism of formation of growth hillocks of large step heights can be suggested on the basis of these observations. The basal seed plates used for the growth experiments were sawed from natural crystals and lap polished. It is a matter of common experience that during cutting, even with an adequate system of cooling, considerable frictional heat is generated near the cutting zone, and thin surface patches of secondary Dauphine twinning often develop (Frondel, 1946). Furthermore, shear produced during lapping operation accelerates the development of an amorphous surface layer (Parrish and Gordon, 1945). It is possible that ring cracks and sets of microfractures having shear offsets of variable magnitude develop near the surface, which remain completely masked by the surface amorphous layer. This layer is removed during the initial heating-up (dissolution) period of the hydrothermal growth runs, the surface cracks and microfractures become exposed, and growth starts at an accelerated rate at these defect sites.

These cracks and microfractures can be visualised as 'giant' screw dislocation centres, giving rise to large growth spires which can be easily observed as type II hillocks under an ordinary microscope. The mechanism proposed is somewhat similar to Frank's model of 'catastrphic buckling' (Frank, 1952), with an important corollary that the localised shear strain developed does not become disseminated by widespread plastic deformation by any slip mechanism, and consequently those 'giant' screw dislocations become stable. Features (A), (B) and (C) of our 'observations' can be explained in this way.

At this stage it is not possible to offer any explanation of features (D) and (E). Frank's suggestion of a pair of dislocations of opposite signs giving rise to terraced structures appears to be untenable here because of (i) single central apex of each terraced hillock (figure 3, plate 15B), (ii) triangular outlines of the terraced hillocks (figures 1 and 3, plate 15) and (iii) coalescence of two growth hillocks showing spires of opposite hands without the formation of any terraced structure (figure 1, plate 15A). It is rather premature to draw any conclusion from feature (F) of our observations since data is too meagre to attach proper significance to them. Experimental arrangements are now being devised to verify the origin of large type II hillocks at those giant' screw dislocation centres.

ACKNOWLEDGEMENTS

The authors are grateful to Shri K. D. Sharma, Director of the Institute, for his kind permission to publish this paper.

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